

Project H-11: Solid state spectroscopic and diffraction studies of TM-doped sodium aluminum hydride

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We continue to probe the molecular basis of the kinetic enhancement exerted by transition metal dopants on the reversible dehydriding of NaAlH_4 to NaH and Al . Previous studies led us to propose that doping results in the substitution of Na by Ti in the bulk hydride lattice. High level calculations recently carried out at the National Institute of Standards and Technology (NIST) show that such bulk substitution is energetically favorable and indicate that substituted Ti is a powerful hydrogen attractor. However, collaborative inelastic neutron scattering studies with Dr. Udovic at NIST did not show any significant differences between the observed vibrational spectra of Ti -doped and pure alanates. It is possible that this discrepancy arises because strong two-phonon scattering occurs at the energies that should be associated with the features that would be expected to arise upon Ti substitution into the system. On the other hand, collaborative infrared spectroscopic studies with the Prof. Yvon at the University of Geneva show that the Al-H stretching frequency of NaAlH_4 is definitely shifted in Ti -doped samples compared to undoped hydride. However, the effect is also observed in samples of NaAlH_4 that undergo prolonged milling without titanium additives.

Continuing collaborative electron paramagnetic resonance studies with Prof. Eaton at the University of Denver have shown that spin isolated Ti(III) is initially the dominant titanium species in the doped hydride. However, recent studies have revealed changes in the populations of the Ti(III) and multi-spin Ti(II) or Ti(0) species upon cycling. These findings are inconsistent with the premise that a single Ti(III) , Ti(II) , or Ti(0) species is responsible for the enhanced hydrogen cycling kinetics as the kinetics do not show any significant change over 100 cycles of dehydrogenation/rehydrogenation. This finding is, however, in agreement with the results of high resolution X-ray diffraction studies that were conducted utilizing the synchrotron light source at ILL in a collaborative effort with Prof. Hauback and Dr. Brinks of the Institute for Energy Technology (IFE). No new phases of any type are observed in samples of uncycled, Ti -doped hydride. However, after several cycles of dehydrogenation/rehydrogenation, a shoulder on the high-angle side of the Al reflections appears that is apparently due to the presence of $\text{Al}_{0.93}\text{Ti}_{0.07}$.

Insight into the mechanistic roll played by the Ti -dopant has been gained through studies of the kinetics of the dehydrogenation of Ti -doped Na_3AlH_6 that were carried out in collaboration with Dr. Kiyobayashi of the National Institute of Advanced Industrial Science and Technology, Japan. Surprisingly, NaAlH_4 and Na_3AlH_6 were found to undergo dehydrogenation at equal rates upon direct doping with titanium. However, much slower kinetics were observed for Na_3AlH_6 arising from the dehydrogenation of Ti -doped NaAlH_4 . These findings can only be understood in context of a model of the hydride in which there is bulk dispersal of the Ti dopant. Furthermore, the dehydrogenation reaction pathways are not sensitive to differences in the Al-H bonding interactions in $[\text{AlH}_4]^-$ and $[\text{AlH}_6]^{3-}$ complex anions. We conclude that the kinetics are instead probably influenced by processes such as nucleation and growth, and/or range atomic transport phenomenon.